Dispersive single-particle excitations in high-Tc copper oxides

doi: 10.1103/PhysRevB.42.2562

Dispersive single-particle excitations in high-T_c copper oxides

H. J. Schmidt* and Y. Kuramoto
Department of Applied Physics, Tohoku University, Sendai 980, Japan
(Received 29 August 1989; revised manuscript received 10 April 1990)

For a Cu_4O_8 cluster with periodic boundary conditions the single-particle excitation spectrum is calculated rigorously by a numerical method with use of a realistic parameter set. The spectrum shows dispersive character at low energies as well as little dispersion at high excitation energies in accordance with experiments using angle-resolved photoemission. The d^8 final state is identified and its energy is found to be close to its experimental one.

In the presence of strong Coulomb repulsion the electronic spectrum can have both dispersive and localized characters. The copper oxide high-T_c superconductors display a typical example of this kind, as was found in angle-resolved photoemission.[1-4] Theoretical calculations of the electronic spectrum have so far been performed with the use of impurity models.[5,6] In order to discuss the dispersive character, however, the lattice periodicity should properly be taken into account. In the present work, we discuss the nature of single-particle excitations by using exact dynamical results for small clusters. We take a Cu_4O_8 cluster as the smallest cluster that still gives information about the momentum dependence of the spectrum.

As the common structural element in high-T_c superconductors we consider a CuO_2 plane containing $3d_{x^2-y^2}$ holes on copper sites and $2p_\sigma$ holes on oxygen sites. We take the following three-band Hubbard Hamiltonian

$$H=-t_{pd}\sum_{(ij)\sigma}(d_{i\sigma}^{\dagger}p_{j\sigma}+\text{H.c.})-t_p\sum_{(jj')\sigma}(p_{j\sigma}^{\dagger}p_{j'\sigma}+\text{H.c.})+\varepsilon_d\sum_{i\sigma}d_{i\sigma}^{\dagger}d_{i\sigma}+\varepsilon_p\sum_{j\sigma}p_{j\sigma}^{\dagger}p_{j\sigma}+U_d\sum_i n_{di\uparrow}n_{di\downarrow}$$
$$+U_p\sum_j n_{pj\uparrow}n_{pj\downarrow}+U_{pd}\sum_{(ij)\sigma\sigma'}n_{di\sigma}n_{pj\sigma'}+K_{\mathrm{HF}}\sum_{(ij)\sigma\sigma'}p_{j\sigma}^{\dagger}p_{j\sigma'}d_{i\sigma'}^{\dagger}d_{i\sigma}\,, \tag{1}$$

where $d_{i\sigma}^{\dagger}$ and $p_{j\sigma}^{\dagger}$ are the creators of d and p holes with energies ε_d and ε_p, t_{pd} and t_p are the hopping constants, and $n_{di\sigma}=d_{i\sigma}^{\dagger}d_{i\sigma}$ and $n_{pj\sigma}=p_{j\sigma}^{\dagger}p_{j\sigma}$ are hole-number operators. The summation (ij) is taken over all Cu–O bonds while the summation (jj') is taken over pairs of neighboring oxygen sites. U_d, U_p, and U_{pd} are on-site and off-site Coulomb interactions. We have included the Hartree-Fock exchange K_{HF} between spins on neighboring Cu and O sites as proposed by Stechel and Jennison.[7] In the Hamiltonian (1) we have made a phase convention such that the hopping terms have the same sign. The momentum $\mathbf{k}_1$ of a hole in (1) to the momentum $\mathbf{k}$ of hole in the model where the phases of the orbitals are equal is shifted by $(\pi/a, \pi/a)$ where a is the lattice spacing. To enable a direct correspondence with experiments we use $\mathbf{k}$ to denote the momentum and we set $a=\pi$ for convenience.

Parameters for the CuO_2 plane have been calculated and discussed by many authors.[6-12] We use the parameters of Hybertsen, Schlüter, and Christensen[9] for La_2CuO_4: $\Delta=\varepsilon_p-\varepsilon_d=3.6$, $U_d=10.5$, $U_p=4.0$, $t_{pd}=1.3$, and $t_p=0.65$ in units of eV. The value for the Hartree-Fock exchange $K_{\mathrm{HF}}=-0.18$ is taken from Stechel and Jennison.[7] A negative K_{HF} favors a triplet of spins on neighboring sites by $2|K_{\mathrm{HF}}|$ compared to a singlet. It therefore reduces the effect of p-d hopping.

Our calculation of the single-particle spectrum is performed in three steps. In the first step the ground state for n holes is obtained by exact diagonalization within the space $S_Z=0$ in the case of even n or $S_Z=\frac{1}{2}$ in the case of odd n. Here S_z is the z component of the total spin. We use the modified Lanczos method[13] which consists of a repeated diagonalization of a 2×2 matrix and gives simultaneously the ground-state energy $E_G^{(n)}$ and wave function $|\Psi_{n0}\rangle$.

In the second step we make a transition to a $n\pm1$ hole state by adding an extra hole to the n-hole ground state or removing one hole. This hole with $S_Z=-\frac{1}{2}$ has a specific momentum and is either from the copper or the oxygen sites. This gives a non-normalized state $|\Psi_A(\mathbf{k})\rangle=A_k|\Psi_{n0}\rangle$, where A_k is the operator of creating or deleting a hole with momentum $\mathbf{k}$. In case of an oxygen hole there are two linear independent choices of a hole state for every $\mathbf{k}$ since there are two oxygens in the unit cell. For $\mathbf{k}=(0,1)$ or $(1,1)$ one of the oxygen holes is nonbonding and we only give results for the bonding oxygen hole that can interact with an added or removed copper hole. For $\mathbf{k}=(0,0)$ both oxygen holes are nonbonding.

In the third step of the calculation the single-particle Green's function

$$G_A(z)=\langle\Psi_A(\mathbf{k})|(z-H)^{-1}|\Psi_A(\mathbf{k})\rangle \tag{2}$$

is calculated in the form of a continued-fraction expansion (CFE).[14] While the CFE is essentially exact for a finite system we truncated its calculation after 100 iterations. At this level there was good convergence in the final result. In the following figures we show the spectral density $\rho_A(\varepsilon)=\pi^{-1}\mathrm{Im}G_A(\varepsilon+E_G^{(n)}-i\delta)$ with a broadening $\delta=0.2$ eV and on a logarithmic scale to make the smaller structures visible. The energy ε is given relative to the energy of the initial state.

The ground states were found to have $\mathbf{k}=(0,1)$ [degenerate with (1,0)] and $S=\frac{1}{2}$ for three and five holes, and $\mathbf{k}=(0,0)$ and $S=0$ for four and six holes. Except for the case of four holes these quantum numbers can be well accounted for by the band theory by successively filling the lowest unoccupied one-hole states. The band theory for our parameters has the (1,1) state lowest with the (0,1) and (1,0) states coming next in energy. The momentum distribution of one-particle states in the four-hole ground state is obtained from the transition probabilities $T_k=\langle\Psi_A(\mathbf{k})|\Psi_A(\mathbf{k})\rangle$ of the single-particle excitations from four to three holes: 43% of the holes have $\mathbf{k}=(1,1)$, 50% have $\mathbf{k}=(0,1)$ or (1,0), and 7% have $\mathbf{k}=(0,0)$. This result shows no big deviation from the band picture. Due to the degeneracy of the (0,1) and (1,0) states the band theory predicts the degeneracy of three singlets and one triplet as four-hole ground states but the electronic correlation splits these states. Since the undoped cluster is insulating as will be discussed later, it is more appropriate to describe the four-hole states by an effective model for the spins on copper sites. Figure 1 shows the calculated spectrum when a d hole is added to the (0,1) ground state with three holes. The lowest four peaks in Fig. 1 have the same quantum numbers as the four lowest levels of a Heisenberg model for a quadratic arrangement of four spins. A final state corresponding to the $S=2$ level of the Heisenberg model cannot be reached from the three-hole ground state with $S=\frac{1}{2}$. Although the undoped ground state, a singlet with $\mathbf{k}=(0,0)$ momentum, is correctly predicted by the Heisenberg model it does not fit the energy splittings shown in Fig. 1 well. A good description of the data must include a cyclic four-spin interaction of considerable size.[15] Such a fit gives a nearest-neighbor exchange $J=0.29$ eV per Cu–Cu bond. This value, however, is much influenced by finite-size effects. We have therefore also studied a Cu_4O_{12} cluster with free boundary conditions and obtained $J=0.13$ eV.[15]

In Figs. 2 and 3 hole removal and addition spectra starting from the four-hole ground state are shown. They correspond to bremsstrahlung isochromat spectroscopy (BIS) and to photoemission spectroscopy (PES), respectively. We have taken $\varepsilon_d=-1.0$ and $\varepsilon_p=2.6$ to guarantee the stability of the initial state against single-particle excitations.

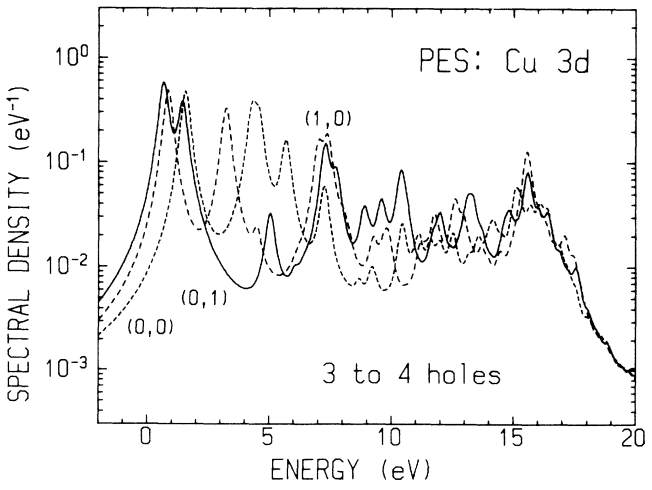

FIG. 1. Spectral density for a hole added to the three-hole ground state with (0,1) momentum. The momentum of the added hole is indicated. The absolute energy is given by $\varepsilon_d=1.0$ eV.

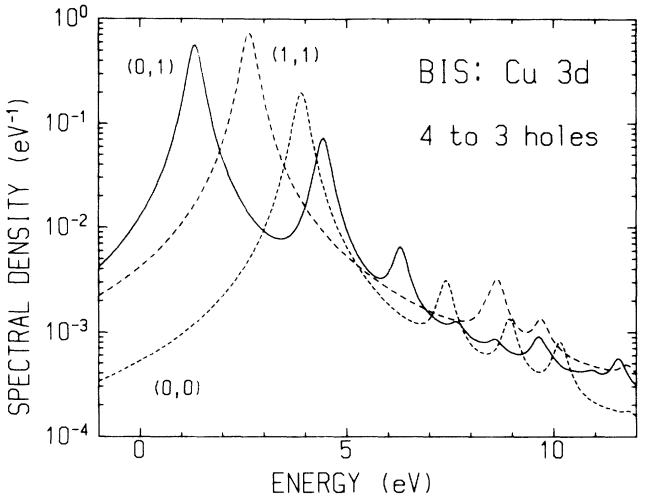

FIG. 2. Spectral density for a copper hole removed from the four-hole ground state (BIS).

The BIS spectra (Fig. 2) show features which are very similar to what is expected from the band theory. There is one main peak for each added momentum. The main peak for a removed (0,0) hole is much smaller than for the other momenta while it is missing in the band picture. The momentum distributions given above can be obtained from the BIS spectra by adding the Cu and O weight for each momentum. The O spectra are not shown here.

The PES spectra (Fig. 3) are more complicated because of the extra correlation effects for the added hole. The spectra show dispersive regions as well as features with no dispersion. The structure at ~ 12.5 eV above the ground state in the Cu spectra [Fig. 3(a)] shows little dispersion. It is identified as a d^8 final state by looking at its shift in energy in a calculation with higher U_d. Its position is very close to the experimentally determined d^8 peak for La_2CuO_4.[16] It is not possible to identify a p^4 final state in the O spectra as shown in Fig. 3(b).

For small excitation energies in Fig. 3 there is a dispersive band followed by a nondispersive peak at ~ 5 eV above the ground state. This feature can be explained if one considers the limit of large Δ and U_d. The lowest five-hole states will have four holes on the copper sites. The fifth hole on the oxygen can be interpreted as a charge-transfer excitation which moves freely and forms a broad band. Making another charge-transfer excitation leads to the obstruction of their movement and to a localized, nondispersive behavior. This explanation also applies to the spectra of a $3\rightarrow 4$ holes transition where the lowest states involve only holes on copper sites. These have been described above by a spin Hamiltonian. Making one charge-transfer excitation gives a dispersive band which again is followed by a nondispersive feature at ~ 6.5 eV above the ground state. For the $3\rightarrow 4$ holes transition the d^8 state with an energy of ~ 15 eV above

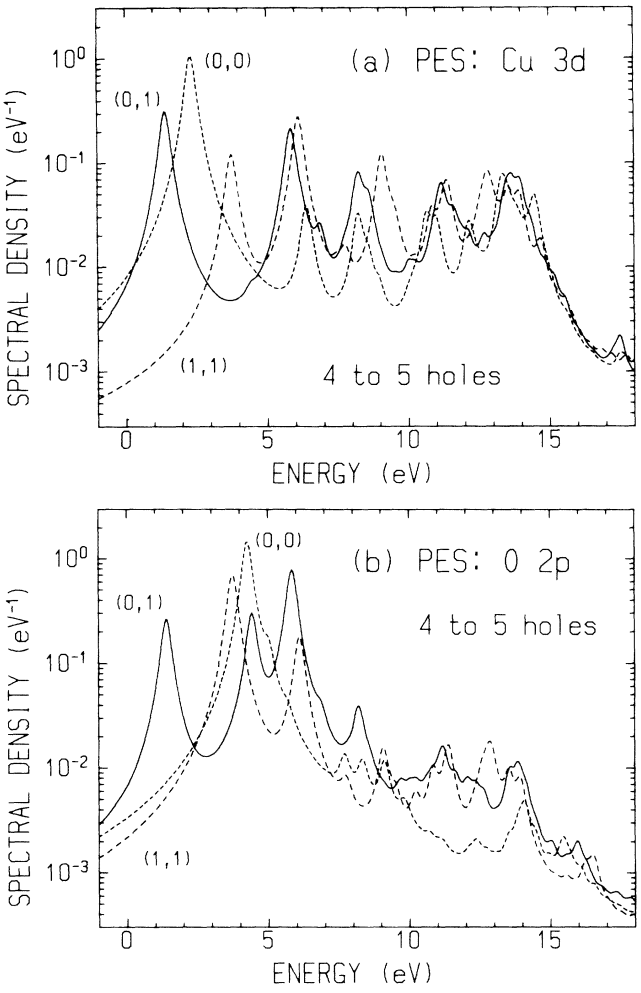

FIG. 3. Spectral density for a hole added to the four-hole ground state (PES). The hole is on (a) copper sites or (b) oxygen sites.

the ground state lies higher than for the 4→ 5 holes transition.

We will now discuss the low-lying band using the band model which predicts an antibonding $2p$-$3d$ band which crosses the Fermi level and leads to a large Fermi surface. This band seems to have been observed in angle-resolved photoemission experiments.[1-4] Electronic correlations, however, renormalize the width of this band. We estimate the bandwidth by taking the splitting between the lowest peaks in Figs. 2 and 3: $W_{\rm PES}\sim(E^{(01)}-E^{(00)})=0.91$ eV and $W_{\rm BIS}\sim(E^{(11)}-E^{(01)})=1.31$ eV, which compares to $E^{(01)}-E^{(00)}=1.36$ eV and $E^{(11)}-E^{(01)}=1.85$ eV for the band theory with the same tight-binding parameters. The reduction of the band width is thus 29% for the BIS and 33% for the PES case. The small difference for the two transitions is due to the fact that the three-hole final states involve fewer holes so that the effects of correlations are smaller. Both U_{pd} and $K_{\rm HF}$ are effectively reducing the Cu-O hopping. We have repeated our calculation with one or two of these parameters set to zero in order to see the size of their influence on the bandwidth. The results are $E^{(01)}-E^{(00)}=0.85$ eV ($U_{pd}=0$), 0.97 eV ($K_{\rm HF}=0$), and 0.91 eV ($U_{pd}=K_{\rm HF}=0$) for the PES case and $E^{(11)}-E^{(01)}=1.43$ eV ($U_{pd}=0$), 1.32 eV ($K_{\rm HF}=0$), and 1.43 eV ($U_{pd}=K_{\rm HF}=0$) for the BIS case.

In striking contrast to the band picture, however, the undoped ground state is insulating in the present result. To show this let us estimate the conductivity gap[17] for removing a hole and inserting it again at a distant position by

$$E_{\rm Gap}^{(n)}=E_G^{(n+1)}+E_G^{(n-1)}-2E_G^{(n)}. \tag{3}$$

In our case it is obtained by adding the energies for the lowest PES and the lowest BIS transitions. For the undoped initial state we get $E_{\rm Gap}^{(4)}=2.8$ eV. This energy gap is reduced from the value $\Delta=3.6$ eV it has for vanishing hybridization, but it is possible to identify the undoped system as a charge-transfer insulator. Without the electronic correlations the conductivity gap vanishes in the undoped case. We notice that $E_{\rm Gap}^{(4)}=2.8$ eV is somewhat larger than the charge-transfer gap of $\sim$2 eV observed in the optical conductivity of La_2CuO_4.[18] The difference may be due to the absence of excitonic effects in the derivation of our result. In contrast to the large conductivity gap in the undoped case evaluating (3) in the doped cases gives $E_{\rm Gap}^{(5)}=0.4$ eV for hole doping and $E_{\rm Gap}^{(3)}=0.2$ eV for electron doping. This is much closer to the value zero it should have for a metal.

Let us discuss the degree of hybridization in the wave function of doped holes. Takahashi *et al.*[2] have claimed that the lowest peaks in photoemission are oxygen peaks by studying their resonant enhancement with varying photon energy. Band-structure calculations, however, give a strongly hybridized antibonding $2p$-$3d$ band at the Fermi level. In our calculation with its strong electronic correlations every copper site has a probability of 70% of having a hole for the undoped case while the value is 15% for each oxygen site. For five holes we get the probabilities 77% (Cu) and 24% (O) which add to $\frac{5}{4}$ holes per unit cell. The PES and BIS transitions between the four- and five-hole ground states has 55% Cu character and 45% O character as is extracted from the relative weight of the lowest O and Cu peak for this transition. For three holes the values for the ground-state occupation are 49% (Cu) and 13% (O) adding to $\frac{3}{4}$ holes per unit cell. The PES and BIS transitions between the three- and four-hole ground states has 80% Cu character and 20% O character as is extracted from the relative weight of the lowest O and Cu peak for this transition.

In conclusion, we have presented the single-particle excitation spectra for a Cu_4O_8 cluster. They show dispersive behavior for low energies. The momentum of the lowest excitation is the same as in the band-theoretical result. The overall bandwidth for the excitations, however, is strongly reduced in comparison with the band theory. We have demonstrated the strong effect of U_{pd} and the smaller effect of $K_{\rm HF}$ on the reduction of the bandwidth. The conductivity gap of the undoped state which is in good agreement with optical experiments shows the breakdown of the band theory. In the region of high excitation energies where the spectra show little dispersion we identified the d^8 final state whose position agrees with photoemission experiments.

*On leave from Institut für Theoretische Physik, Universität zu Köln, D-5000 Köln 41, Federal Republic of Germany.

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